Deposition of Microcrystalline Silicon Materials and Solar Cells Using the HWCVD and Pulsed PECVD Techniques

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ABSTRACT

Several techniques have shown promise in depositing microcrystalline silicon (μc-Si), including VHF-PECVD, Hot Wire CVD, and Pulsed PECVD. Previously, we had developed a new HWCVD approach (US Patent number 6,214,706 B1) which uses a graphite filament to address some of the technique's problems, specifically longevity of the filament and reproducibility of the material produced. With the new technique, it has been found possible to deposit μc-Si material that is entirely (220) oriented, with no visible (111) orientation in the XRD spectra. We report on the incorporation of this μc-Si material into solar cell devices, and compare their performance with similar devices deposited by tantalum-HWCVD. We also report on the deposition of microcrystalline Si materials and devices via the Pulsed PECVD technique. The crystallite orientation of the films changes from a random orientation to a (220) orientation near the microcrystalline-to-amorphous transition. The observed change in orientation (220 vs. 111) is correlated with solar cell performance, with the best efficiency seen for (220) oriented i-layers. The role of ion bombardment and grain boundary interfaces on device performance is also investigated.

1. Introduction

Microcrystalline silicon (μc-Si) has attracted attention in recent years because of the material's stability under illumination. In this paper, we examine μc-Si deposited both by the "Hot Wire" chemical vapor deposition (HWCVD) technique and by the Pulsed PECVD techniques.

Previously, we have reported on our development of a new HWCVD technique using a graphite filament (C-HWCVD)[1,2] that addresses some of the technique's problems, specifically longevity of the filament as well as reproducibility of the deposited films. In this paper, we extend the C-HWCVD to the deposition of μc-Si films and examine the differences with μc-Si films deposited by the HWCVD technique using Ta wire.

The Pulsed PECVD technique is a modification of the typical 13.56 MHz PECVD deposition technique. In this technique, the plasma is modulated in the range of 1 to 100kHz and with an ON-time to OFF-time ratio of 10-50%, so that negatively charged particles can be extracted before they grow to sizes that can cause manufacturing yield problems. In this paper, we examine the use of the technique in depositing μc-Si p/i/n devices.

2. Experimental Methods

Microcrystalline silicon (μc-Si) films were produced in a commercially available PECVD/HWCVD system specifically designed for the thin film semiconductor market and manufactured by MVSystems,Inc. This chamber is capable of depositing in either the PECVD or the HWCVD mode of operation without breaking vacuum on 10 cm X 10 cm substrates situated on either the anode side of the RF electrode assembly (for the PECVD) or above the moveable HWCVD assembly.

Simple solar cell structures of n-i-p and p-i-n configuration were constructed with the μc p -type material fabricated using a SiH_4, H_2, and Trimethylboron gas mixture. The typical dark conductivity of the p-type μc material was 1 x 10^{-1} $(Ohm\text{-}cm)^{-1}$. The μc n+ layer was prepared using a SiH_4, H_2, and PH_3 gas mixture. The resultant n+ material exhibited a dark conductivity of 2 $(Ohm\text{-}cm)^{-1}$. The n-i-p devices were deposited onto 1737 glass or Asahi TCO substrates coated with 3000 Angstroms of Mo, while the p-i-n devices were deposited onto Asahi tin oxide coated glass with a layer of zinc oxide. For the top contact of the n-i-p structures, semi-transparent Ag was used, while for the rear contact of the p-i-n devices opaque Ag was used. The opto-electronic, structural, and impurity properties were characterized by photo- (σ_{ph}) and dark conductivity (σ_d), FTIR, and SIMS techniques.

3. Results and Discussion

C-HWCVD Technique

Microcrystalline silicon was deposited using a conventional Ta-filament HWCVD method, with the primary parameter variations being the hydrogen dilution and substrate temperature. The R_{220} values for the films near the microcrystalline-to-amorphous transition showed values of over 700%, indicating a strong (220) orientation in the film. (The R_{220} value is the ratio of the (220) peak area to the (111) peak area.) By way of comparison, randomly oriented silicon powder shows an R_{220} value of 55%. This (220) orientation has been found to correspond to a columnar structure in the deposited film, and this type of film structure is believed to be more suitable for solar cell applications, as the grain boundaries are oriented parallel to the primary direction of current flow.

Microcrystalline Si films have also been deposited using a graphite filament (C-HWCVD), and a sample film's X-Ray diffraction spectrum is shown in Fig. 1. For this film, there is no detectable microcrystalline peak corresponding to the (111) phase. This type of very strong

(220) orientation has also been observed by M. Schubert's group in Stuttgart [3] working on C-HWCVD in conjunction with MVSystems, Inc.

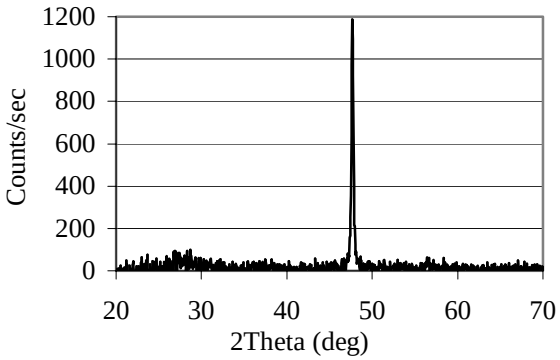

Fig. 1: XRD Spectrum of μc-Si film deposited via C-HWCVD. (Corrected for substrate)

Pulsed PECVD Technique

We now turn to the data for the solar cell devices with the i-layer deposited by Pulsed PECVD. Figure 2 shows the fill factor as a function of hydrogen dilution for n-i-p structures deposited on TCO/Mo substrates at two different substrate temperatures. The thickness of the i-layer in these devices was about 0.9 microns. The pressures used for these devices were typical of those used in amorphous silicon deposition (~500 mTorr). The J_{SC} values, corrected for the semi-transparent Ag top contact, were 10-12 mA/cm^2 over the regime studied. The V_{OC} of these devices were also low, less than 300 mV for all devices in this regime. As with the HWCVD films, the pulsed PECVD films exhibit the strongest (220) orientation near the microcrystalline-to-amorphous transition. Comparing the single films and the devices, the devices deposited in the region of strong (220) orientation exhibit the best fill factor. Increasing the hydrogen dilution causes the films to become more randomly oriented, with a corresponding decrease in the fill factor. This decrease is presumably due to increased carrier recombination in the intrinsic layer.

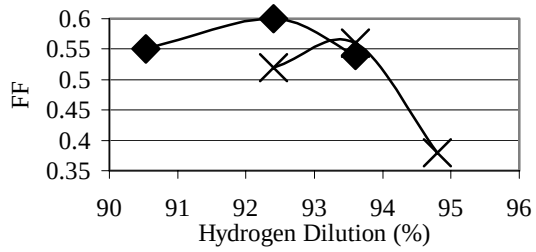

Fig. 2: Fill Factor as a function of hydrogen dilution for n-i-p μc-Si devices with i-layer deposited via the pulsed PECVD technique. Diamonds = 325 C, Crosses = 210 C

Devices of p-i-n structure were also deposited on textured Asahi TCO coated with a thin layer of zinc oxide. These i-layers were deposited at higher pressures than the n-i-p devices shown in Fig. 2. This ZnO layer is intended to prevent reduction of the Asahi TCO during the deposition of the μc-p layer. Figure 3 shows the I-V curves for two p-i-n devices with a 7000 Å i-layer. The only difference between the two devices is that one of the devices (solid line) has a nucleation layer inserted between the μc-p and μc-i layers. The efficiency of the nucleated device is 3.7%.

By inserting an intrinsic layer with a high nucleation density, the device shows an improvement in every parameter. The quantum efficiency measurements of the nucleated devices indicate an increased collection for λ>800 nm, which indicates that the crystalline fraction of the i-layer has been improved. Further improvements in the nucleation layer as well as the crystalline fraction of the p-layer have resulted in a device with an efficiency of ~5%. This device efficiency is awaiting confirmation at NREL.

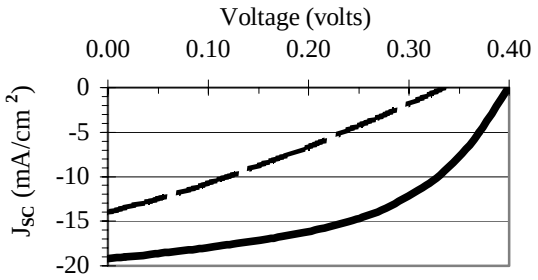

Fig. 3: White I/V measurements of two p-i-n structures with i-layer thickness of 7000 Angstroms. Intrinsic layer deposited by Pulsed PECVD technique at high pressures (>1 Torr). Dashed line indicates no nucleation layer between p, i layers, solid line indicates nucleation layer between p, i layers

4. Conclusions

We have demonstrated that the C-HWCVD technique is capable of depositing μc-Si films that are entirely (220) oriented. Microcrystalline silicon films and devices have been deposited using a pulsed PECVD technique. Using this technique, μc p-i-n devices of greater than 4% efficiency have been deposited.

5. Acknowledgements

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